

PROCEEDINGS
OF THE
NATIONAL ACADEMY OF SCIENCES
INDIA
1949

PART I]

SECTION A

[VOL. 18

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ALLAHABAD

PUBLISHED BY THE COUNCIL

Price Rs. 5 (India) : Rs. 5/8 (Foreign)

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HUMUS AND COAL AS MANURES

By

N. R. DHAR

**Manuring with Nitrogen Rich Compounds and Loss of
Nitrogen**

From ancient times animal matter like blood, fish, bone meal, tankage, wool-residues, meat-residues, guano, human excreta etc. has been used as manure, but the mechanism of their action has been cleared up only in recent years. The carbon-nitrogen ratio of these substances is less than 10 and when they are mixed with soil, the carbonaceous compounds and the proteins are oxidized with the liberation of carbondioxide and ammonia, which in its turn is further oxidised to nitrite and nitrate, which is the chief plant food material. The above mentioned substances are known to be fairly quick acting manures in crop production. Researches carried on in the Allahabad University have established that when nitrogenous fertilizers are added to the soil, a good deal is wasted as nitrogen gas without benefit to the crop or soil. When 100 lbs of ammonium sulphate are added per acre of land under cultivation, about 40 lbs are available to the crop, but 60 lbs are wasted as nitrogen gas under ordinary conditions of cultivation. In our recent experiments the following results have been obtained with different nitrogenous substances :—

| Substances mixed with soil | Period of exposure | Loss of nitrogen % | | Percentage loss of nitrogen in unit time (per month) | |
|----------------------------|--------------------|--------------------|-------|--|-------|
| | | Light. | Dark. | Light. | Dark. |
| (1) Ammonium Sulphate. | 2 months | 55.5 | 43.2 | 27.8 | 21.6 |
| (2) Ammonium Phosphate. | " | 67.5 | 58.4 | 33.8 | 29.2 |
| (3) Ammonium Nitrate. | " | 28.9 | 21.0 | 14.5 | 10.5 |
| (4) Ammonium Tartrate. | " | 47.6 | 38.3 | 23.8 | 19.2 |
| (5) Ammonium Oxalate | " | 36.6 | 28.6 | 18.3 | 14.3 |
| (6) Ammonium Citrate | 4½ months | 69.3 | 54.8 | 22.1 | 12.2 |
| (7) Urea | 5½ months | 47.4 | 35.1 | 10.5 | 7.8 |
| (8) Hippuric Acid | 4½ " | 42.3 | 23.2 | 9.4 | 5.2 |
| (9) Gelatine | 4½ " | 40.1 | 23.2 | 8.9 | 5.2 |
| (10) Oil-Cake | 5½ " | 35.9 | 29.0 | 6.5 | 5.3 |
| (11) Blood | 6 " | 54.1 | 48.7 | 9.0 | 8.1 |

The amount of nitrogen initially present in the above nitrogenous compounds varied from about 0.25 gram to 0.5 gram in 100 grams of soil. Moreover, with such manures acidity is produced. With ammonium nitrate better result is expected and obtained because half of the nitrogen is in the form of nitrate and hence the

loss is less than with ammonium sulphate. With ammonium nitrate no acidic residue is added to the soil permanently as the nitrate ion is either absorbed by the plant or leached away in the underground soil. With sodium or potassium nitrate certainly better results are expected but when the carbonaceous substance in the soil is large, there is always the possibility of the formation of nitrite and perhaps ammonium salt and thus loss of nitrogen as nitrous acid and nitrogen gas specially in acid soils and there is considerable leaching with nitrates. Hence these inorganic fertilizers although they are quick-acting and readily available in our industrial civilisation, do not enrich the soil permanently as there is hardly any addition of humus with such fertilizers. The great advantage with such fertilizers is that they can be added to the growing crop or as a top-dressing material and no time interval is needed between the addition of the fertilizer and the sowing of the crop. The disadvantages are (1) much loss of nitrogen in the gaseous state specially with ammonium compounds (2) the production of acidity (3) leaching (4) no humus addition (5) and specially in our soil which is on the alkaline side, there is the possibility of a loss as ammonia gas.

Fixation of Atmospheric Nitrogen in Soil and Formation of Humus

For over twenty-five years we have been utilising different energy producing materials in enriching the soil from the nitrogen point of view. We have tried all the sugars and observed that when they are mixed with soil, they are oxidised finally into carbondioxide and water with the liberation of energy which is utilised in fixing the nitrogen of the air on the soil surface. If the system is illuminated by sunlight or artificial light, the light is absorbed by the system and the nitrogen fixation is greatly increased. This utilisation of light in enriching the soil takes place under natural conditions all over the world and appears to be next in importance to photosynthesis in plants. We have utilised all sugars, starch, glycerol, filterpaper, lignin, butter, melted and clarified butter known as *Ghee*

in India, and found that all these materials though free from nitrogen undergo oxidation in soil in presence and absence of sunlight. In all these cases the nitrogen addition to the soil takes place without the addition of nitrogenous manures. We have also observed that molasses, press mud, plant-residues, leaves, farm-yard manure, cow-dung, straw, saw-dust etc. with carbon/nitrogen ratio varying from 100 to 15 not only add the nitrogen they contain but fix atmospheric nitrogen as well. The fixation of nitrogen is greater, the greater the carbon/nitrogen ratio of the energy material. In this process also sunlight or artificial light is utilised in increasing the nitrogen status. Marked fixation also takes place under sterile conditions.

It is interesting to note that greater nitrogen fixation is observed with wheat straw than Neem leaf (*Melia Azadiractta* Lina). Cow-dung comes third in order, the efficiency of nitrogen fixation (amount of nitrogen fixed per gram of carbon oxidized) being 24.8 with wheat straw, 21.5 with Neem leaf, 20.3 with cowdung in sunlight. In the dark the efficiency is less than half. This behaviour can be explained from the difference in their carbon-nitrogen ratio.

The carbon-nitrogen ratio of the materials are recorded below :—

| Substances | Total Carbon% | Total Nitrogen% | C/N ratio |
|--|---------------|-----------------|-----------|
| (1) Cowdung | 8.06 | 0.414 | 19.44 |
| | 9.37 | 0.422 | 22.20 |
| | 6.52 | 0.362 | 18.00 |
| | | Mean | 19.88 |
| (2) Neem leaf. (<i>Melia Azadiractta</i> Lina). | 21.31 | 0.670 | 31.8 |
| | 18.57 | 0.654 | 28.4 |
| | 17.98 | 0.642 | 28.0 |
| | | Mean | 29.4 |
| (3) Wheat straw | 38.06 | 0.5742 | 66.3 |
| | 38.06 | 0.5707 | 66.6 |
| | | Mean | 66.45 |

It is clear that the greater the carbon-nitrogen ratio of the material, the greater is the efficiency of fixation of nitrogen.

On the application of farmyard manure in Rothamsted for a number of years the soil nitrogen which was originally 0.122% rose to 0.236% from 1842 to 1914. Repeated additions of ammonium sulphate or sodium nitrate did not improve the nitrogen status of soils at all. Similar results as recorded below were obtained by us at Allahabad. Moreover there is more nitrogen in the soil covered with grass than when there is no grass cover :—

| Soils | Total C% | Total N% | NH ₃ -N% | NO ₃ -N % |
|--|----------|----------|---------------------|----------------------|
| (1) Not covered with grass. | 0.386 | 0.0388 | 0.0024 | 0.0012 |
| (2) Covered with grass for 6 months | 0.633 | 0.0630 | 0.0039 | 0.0021 |
| | 0.658 | 0.0656 | 0.0039 | 0.0029 |
| (3) Covered with grass for the whole year. | 0.790 | 0.0786 | 0.0051 | 0.0025 |

It is interesting to note that the percentage of nitrogen in the fields rose from 0.0386 to 0.094 after the first application of cowdung and to 0.1517% on the second addition and to 0.2000% after the third application of cowdung. The corresponding results with Neem leaf are as follows :—

| | | | | |
|---------------------------|-----|-----|-----|---------|
| Original nitrogen content | ... | ... | ... | 0.0386% |
| After first application | ... | ... | .. | 0.0628% |
| After second application | .. | ... | .. | 0.0815% |
| After third applicatipn | .. | ... | ... | 0.1021% |

The foregoing results show conclusively that repeated application of cowdung and neem leaf enrich the soil markedly by increasing its nitrogen content and humus by fixation of nitrogen and retaining the added nitrogen as well, i.e., the nitrogen of the materials added.

It is estimated that 35 billion kilograms, i.e., 34750 million tons of cellulose containing 13750 million tons of carbon are added every year to the earth. From our experiments we find that 40 % of the

carbon is oxidised in our climatic conditions in four or five months and even if the same amount be taken to be oxidised on the surface of the earth in the whole year, it would mean that 5500 million tons of carbon are oxidised every year. On a moderate estimate of 15 mgms. nitrogen fixation per gm. of carbon oxidised in sunlight about 82.5 million metric tons of nitrogen are added to the earth by fixation provided 40 % of the carbon added is oxidised. We can conclude that out of total 82.5 million tons at least 50%, i.e., 41.25 million tons of nitrogen are fixed in soils by absorption of solar light. The total output of nitrogen fixed synthetically in the factories of the world in 1937 was 3.54 million tons, i.e., 1/12th. of what is obtained by fixation under natural conditions by the utilization of sunlight.

It is interesting to note that although the velocity of oxidation of organic matter in sterile condition is smaller than in unsterile conditions, the efficiency of nitrogen fixation in sterile conditions is of the same order as that obtained in the unsterile experiments as is clear from the following data :—

| Condition | Material used | Period of exposure (Months) | Carbon oxidized % during the whole period | Carbon oxidized % during one month | Amount nitrogen fixed in mgm. per 100 gms of soil | Efficiency in sunlight |
|-----------|---------------|-----------------------------|---|------------------------------------|---|------------------------|
| Unsterile | Cowdung | 4 | 0.475 | 0.119 | 9.8 | 20.7 |
| Sterile | Cowdung | 4 | 0.303 | 0.076 | 4.6 | 15.2 |
| Unsterile | Neem leaf | 4 | 0.402 | 0.101 | 9.1 | 22.6 |
| Sterile | Neem leaf | 4 | 0.221 | 0.055 | 2.8 | 17.2 |
| Unsterile | Wheat straw | 12 | 0.605 | 0.050 | 14.2 | 23.8 |
| Sterile | Wheat straw | 12 | 0.319 | 0.026 | 5.5 | 17.4 |

Influence of Light on Nitrogen Fixation by *Azotobacter* in Presence of Calcium Carbonate

In 1941 Dhar and Seshacharyulu (Proc. National Academy of Sciences, India 1941, **11**, 97) reported the fixation of 11.75 milligrams of nitrogen in light and 18.5 milligrams in the dark in 100 cc of mannitol in tap water containing 2 grams mannitol, 0.02 gm dipotassium hydrogen phosphate and 1 gram calcium carbonate containing a pure culture of *Azotobacter* after exposure for sixty-three days to sunlight and a comparative set covered with black cloth. At that time the carbon remaining unacted upon was not estimated and hence the efficiency, i.e., the amount of nitrogen fixed per gram of carbon oxidised could not be determined. Recently Dhar and Ghildyal have extended these experiments and have obtained the following results using the same medium after inoculating with an *Azotobacter* culture :—

After 6 month's exposure in April to September 1949. 500 cc containing the above materials and *Azotobacter* were used in these experiments

LIGHT

Carbon oxidised—1.3 gram.

Nitrogen fixed—20.8 milligrams.

Efficiency —16 milligrams.
per gram of carbon
oxidised.

DARK

Carbon oxidised—1.4 gram.

Nitrogen fixed—17.5 mgms.

Efficiency—12.5 mgms.
per gram of carbon
oxidised.

After 65 days' exposure in November, December 1949 and January 1950.

LIGHT

Carbon oxidised—2.02 grams

Nitrogen fixed—25 milligrams.

DARK

Carbon oxidised—2.17 grams.

Nitrogen fixed—24 milligrams.

Efficiency per—12.4 milligrams.
gram of carbon
oxidised.

Efficiency per—11 milligrams.
gram of carbon
oxidised.

After 110 days' exposure in November, December 1949 and January and February 1950.

LIGHT

DARK

Carbon oxidised—2.174 grams.

Carbon oxidised—2.011 grams.

Nitrogen fixed—19.75 mgms

Nitrogen fixed—16 milligrams.

Efficiency —9 mgms per gram
of carbon oxidised.

Efficiency—7.9 mgms per gram
of carbon oxidised.

In the last two sets of experiment, the carbon added as mannitol was 3.054 gms but the whole was not oxidised even in 110 days.

It is clear, therefore, that the efficiency of nitrogen fixation in presence of calcium carbonate with a culture of *Azotobacter* fed with mannitol is appreciably greater in light than in the dark due to the absorption of light by calcium carbonate although the carbon oxidized in two cases is slightly less in light than in the dark.

Humus in composts is less than in direct addition of plant materials to soil without composting.

The composts prepared according to the Indore method contain about 0.9 % nitrogen and about 13% carbon and potash, phosphate and other minerals. In other words, if one ton of such a compost is added per acre of land, we are adding approximately 18 lbs of nitrogen and about 220 lbs of carbon as humus and some potash, phosphate and other minerals. A part of the nitrogen of the compost is actually available to the crop. One ton of such compost per acre does not provide the adequate quantity of nitrogen for a good crop yield. On the other hand, if one ton of wheat straw containing 0.6 % nitrogen is added to the soil before composting it adds 13 lbs of nitrogen and 1000 lbs of carbon. A good deal of this carbon is oxidised in three or four months. This may lead to the fixa-

tion of about 20 lbs of additional nitrogen. Hence, 1 ton of undecomposed wheat straw adds to the soil almost double the nitrogen and humus obtained with the composted material. But in this case a time interval should be given between the addition of straw and the growing of a crop.

In other words, a new method of manuring land with carbohydrates, celluloses, lignins or any energy material with a carbon/nitrogen ratio much greater than 10 has been developed. So far materials with carbon nitrogen ratio greater than 10 were allowed to ferment and undergo oxidation as in composting, and when the carbohydrates and other energy materials were partially oxidised and the carbon/nitrogen ratio of the materials approached 10, the product was used as a compost in top-dressing in cultivation. But we have been able to establish that all energy materials when added to the soil enrich it from the humus and nitrogen point of view and in this process the energy of oxidation as well as solar light is utilised for soil improvement, by fixing the nitrogen of air and this is the chief source of soil nitrogen all over the world.

With substances like urea, blood, guano, gelatine, wool-residue etc., the carbon/nitrogen ratio being less than 10, favourable effect to crop production is observed when the crops are grown within two or three weeks after the addition of such manures. With these manures also there is a marked loss of nitrogen in the gaseous state although there is the formation of a certain amount of humus depending on the carbon/nitrogen ratio of the manure. The greater the carbon/nitrogen ratio of the starting materials the greater is the production of humus and greater is the residual effect.

Oil-cake should be cheap in tropical countries and should prove to be a good manure as the carbon-nitrogen ratio of most oil-cakes is of the order 10:1, *i.e.*, the composition is practically the same as that of soil humus, but the difficulty of the oil-cake is that the oils present in such cakes are oxidised in the soil with great difficulty. It seems that they form oleates, palmitates, stearates of calcium, iron, aluminium etc. which are very sparingly soluble in water and are

not readily oxidised. Since the carbon/nitrogen ratio is practically that of soil humus and because the oil-cakes remove the alkalinity of our soils which are on the alkaline side as in the north of India, they should be extensively used in this country provided the price is not too high. They contain 5—7% nitrogen and can readily fix nitrogen when mixed with either molasses or plant leaf.

Humus Formation with Soluble Carbohydrates, Glycerol and Fats.

Molasses, press-cakes and other waste materials of sugar industry can fix nitrogen readily in our soils within a month or so. With alkali soils they are specially beneficial. Although there is no cellulose or lignin in such materials but there is appreciable humus formation and residual effect because of the formation of unstable compounds containing carbohydrates and proteins. The proteins are formed by nitrogen fixation either through the intervention of micro-organisms or from physico-chemical agencies. The generally accepted view is that humus consists chiefly of ligno-proteins but the humus obtained from molasses is a good source of nitrogen to crops and creates residual effect in soils, specially marked in paddy cultivation. In the animal body the whole of the carbohydrate ingested is not oxidised but a part is preserved as glycogen. It is worth while examining whether the glycogen is in combination with the body or food protein or not. We have frequently observed that when molasses is added to our soils neutral or alkaline either in fields or in dishes the C/N ratio which after the addition of molasses may be very high but it tends to become 10:1 in course of time showing the formation of humus in such soils. Similarly when glycerol or any other carbohydrate or fats are added, the carbon/nitrogen ratio converges to 10:1 in time, although, the quantities of carbon and nitrogen present are greater than those in the original soil. Hence humus formation is possible with carbohydrates, glycerol, fats etc. as with cellulosic materials, lignins, cotton-wool, filter-paper, leaves etc.

No Decrease in Available soil Nitrogen on Addition of Sugars, Starch and Glycerol to Tropical soil.

The most important point with soluble carbohydrates, glycerol and starch as manures in tropical soil is that the available nitrogen goes on increasing from the very beginning, the ammoniacal nitrogen goes on increasing steadily, the nitrate nitrogen never goes down, remains stationary for some time, but increases later on. This behaviour of soluble carbohydrate manuring in our country is in marked contrast to the existing literature in Europe and in Hawaii where marked fall of nitric nitrogen has been observed on the addition of sugar to soil. With cellulosic or ligno-cellulosic materials and fats in tropics there is an initial fall of ammoniacal and nitric nitrogen. The manuring value of soluble carbohydrates is much quicker than with celluloses, lignins and fats, as will be evident from the following tables:—

Plots 4 feet × 4 feet Containing 10 kgms molasses

LIGHT

| Date | NH ₃ -N % | NO ₃ -N % | Total N% | Total carbon % | Azotobacter per gm of dry soil in millions. | Total Bacteria per gm of dry soil in milli- ons. |
|-------------------------------|-------------------------|-------------------------|-------------|----------------------|---|---|
| 13-2-1937. (Original soil) | 0.0006 | 0.0014 | 0.0310 | 0.3472 | 0.9 | 12.0 |
| 9-3-1937 | 0.0012 | 0.0016 | 0.0344 | 1.7708 | 12.5 | 38.0 |
| 26-4-1937 | 0.0016 | 0.0016 | 0.0388 | 1.4136 | 75.0 | 245.0 |
| 12-7-1937 | 0.0028 | 0.0016 | 0.0456 | 0.6875 | 155.0 | 385.0 |
| 25-9-1937 | 0.0019 | 0.0017 | 0.0461 | 0.4728 | 115.0 | 305.0 |

Nitrogen fixed per gram of carbon oxidised—8.9 mgm

DARK

| Date | NH ₃ -N % | NO ₃ -N % | Total N% | Total carbon % | Azotobacter per gm of dry soil in millions | Total bacteria per gm of dry soil in milli- ons. |
|------------------------------|-------------------------|-------------------------|-------------|----------------------|--|---|
| 13-2-1937 (Original soil) | 0.0006 | 0.0012 | 0.0300 | 0.3240 | 1.0 | 13.0 |
| 9-3-1937 | 0.0010 | 0.0015 | 0.0328 | 1.7732 | 16.0 | 48.0 |
| 26-4-1937 | 0.0013 | 0.0015 | 0.0394 | 1.4702 | 120.0 | 365.0 |
| 12-7-1937 | 0.0014 | 0.0015 | 0.0375 | 0.7854 | 290.0 | 615.0 |
| 25-9-1937 | 0.0013 | 0.0016 | 0.0388 | 0.4468 | 315.0 | 645.0 |

Nitrogen fixed per gram of carbon oxidised—3.56 mgm.

1 Kilogram of soil plus 20 grams of filter paper*LIGHT*

| Date | NH ₃ -N % | NO ₃ -N % | Total N% | Total carbon% | Moisture % | Azotobacter per gm of dry soil in millions. |
|-------------------------------|-------------------------|-------------------------|-------------|------------------|---------------|---|
| 30-10-1936 (Original soil) | 0.0011 | 0.0020 | 0.0540 | 0.567 | 2.2 | 2.4 |
| 22-12-1936. | 0.0008 | 0.0018 | 0.0540 | ... | 3.8 | 3.7 |
| 20-1-1937. | 0.0007 | 0.0016 | 0.0560 | ... | 3.1 | 7.7 |
| 20-3-1937. | 0.0006 | 0.0014 | 0.0583 | ... | 3.0 | 12.5 |

| Date | NH ₃ N% | NO ₃ -N % | Total N% | Total carbon% | Moisture % | Azotobacter per gm of dry soil in millions. |
|------------|--------------------|-------------------------|-------------|------------------|---------------|---|
| 7-5-1937. | 0.0006 | 0.0012 | 0.0664 | ... | 3.5 | 20.5 |
| 7-6-1937, | 0.0006 | 0.0011 | 0.0677 | ... | 3.1 | 27.2 |
| 8-7-1937. | 0.0007 | 0.0014 | 0.0666 | 0.7012 | ... | 18.0 |
| 13-9-1937. | 0.0014 | 0.0021 | 0.0646 | 0.6704 | ... | 12.0 |

Nitrogen fixed per gram of carbon oxidised—18.1 mgm (Calculated)

1 Kilogram of soil plus 20 gms filter paper.

DARK

| Date | NH ₃ N% | NO ₃ -N % | Total N% | Total carbon% | Moisture % | Azotobacter per gm of dry soil in millions. |
|-------------------------------|--------------------|-------------------------|-------------|------------------|---------------|---|
| 30-10-1936 (Original soil) | 0.0011 | 0.0020 | 0.0540 | 0.5670 | 2.2 | 2.4 |
| 22-12-9136 | 0.0007 | 0.0015 | 0.0540 | | 4.8 | 4.3 |
| 20-1-1937 | 0.0006 | 0.0012 | 0.0540 | | 4.2 | 5.7 |
| 20-3-1937 | 0.0006 | 0.0010 | 0.0552 | | 4.0 | 25.5 |
| 7-5-1937 | 0.0006 | 0.0009 | 0.0567 | | 3.0 | 60.0 |
| 7-6-1937 | 0.0006 | 0.0009 | 0.0575 | | | 80.0 |
| 8-7-1937 | 0.0007 | 0.0009 | 0.0583 | | | 92.5 |
| 13-9-1937 | 0.0008 | 0.001 | 0.0608 | 0.6486 | | 145.0 |

Nitrogen fixed per gm of carbon oxidised—9.2 mgm (Calculated)

1 Kilogram soil plus 20 gms butter*LIGHT*

| Date | NH ₃ -N % | NO ₃ -N % | Total N % | Total carbon % | Moisture % | Azotobacter per gram of dry soil in millions. |
|-------------------------------|----------------------|----------------------|-----------|----------------|------------|---|
| 13-10-1936 (Original soil) | 0.0014 | 0.0032 | 0.0570 | 0.6156 | 1.8 | 5.1 |
| 14-11-1936 | 0.0015 | 0.0032 | 0.0570 | 1.4195 | 2.6 | 5.8 |
| 15-12-1936 | 0.0016 | 0.0032 | 0.0570 | 1.3883 | 3.1 | 7.6 |
| 13-1-1937 | 0.0014 | 0.0029 | 0.0570 | 1.3497 | 3.5 | 9.5 |
| 18-2-1937 | 0.0009 | 0.0024 | 0.0591 | 1.1968 | 3.0 | 12.0 |
| 11-5-1937 | 0.0007 | 0.0011 | 0.0617 | 0.9381 | 3.0 | 35.0 |
| 11-9-1937 | 0.0006 | 0.0010 | 0.0646 | 0.6659 | 3.0 | 25.0 |
| 12-10-1937 | 0.0009 | 0.0011 | 0.0626 | 0.6318 | 3.2 | 15.6 |

Nitrogen fixed per gram of carbon oxidised—10.07 mgms.

1 Kilogram soil plus 20 grams butter.*DARK*

| Date | NH ₃ -N % | NO ₃ -N % | Total N % | Total C % | Moisture % | Azotobacter per gram of dry soil in millions. |
|-------------------------------|----------------------|----------------------|-----------|-----------|------------|---|
| 13-10-1936 (Original soil) | 0.0014 | 0.0032 | 0.0570 | 0.6156 | 1.8 | 5.1 |
| 14-11-1936 | 0.0014 | 0.0032 | 0.0570 | 1.4564 | 3.9 | 6.6 |

| Date | NH ₃ -N % | NH ₃ -N % | Total N % | Total % Carbon | Moisture % | Azotobacter per gm of dry soil in millions. |
|------------|-------------------------|-------------------------|--------------|----------------------|---------------|---|
| 15-12-1936 | 0.0015 | 0.0030 | 0.0570 | 1.4278 | 4.0 | 8.5 |
| 13-1-1937 | 0.0002 | 0.0028 | 0.0570 | 1.3962 | 4.4 | 14.6 |
| 18-2-1937 | 0.0007 | 0.0021 | 0.0583 | 1.2854 | 4.0 | 20.0 |
| 14-5-1937 | 0.0006 | 0.0010 | 0.0591 | 1.0952 | 4.0 | 50.0 |
| 11-9-1937 | 0.0006 | 0.0900 | 0.0600 | 0.7456 | 3.5 | 70.0 |
| 12-10-1937 | 0.0007 | 0.0009 | 0.0591 | 0.6036 | 3.8 | 58.8 |

Nitrogen fixed per gram of carbon oxidised—4.22 mgm.

Nitrogen Fixation and Humus Formation are Quicker and Greater in sandy soils than in clay soils

When sand is used as medium, the nitrogen fixation is much greater than with soil as the nitrogen content of sand is much smaller than that of soil. The following results have been obtained using sand as a medium :—

100 gms sand with different amounts of energy materials.

Exposure 2½ months.

| Substance | %C Initial | %N Initial | %C Final | %N Final | Efficiency i. e. nitro- gen fixed in milligrams per gram of carbon oxidised |
|---------------|---------------|---------------|-------------|-------------|---|
| Butter Light | 1.2846 | 0.0101 | 1.0625 | 0.0164 | 28.3 |
| „ Dark | 1.2846 | 0.0101 | 1.1543 | 0.0122 | 15.9 |
| Lactic Light | 1.3113 | 0.0104 | 1.0066 | 0.0181 | 25.3 |
| acid Dark | 1.3113 | 0.0104 | 1.1387 | 0.0130 | 14.8 |
| Mustard Light | 1.3099 | 0.0148 | 1.0388 | 0.0221 | 26.5 |
| oil Dark | 1.3099 | 0.0148 | 1.1634 | 0.0169 | 14.1 |

Exposure 5 months.

| | | | | | |
|---------------|--------|--------|--------|--------|------|
| Butter Light | 1.2846 | 0.0101 | 0.8540 | 0.0228 | 27 |
| „ Dark | 1.2846 | 0.0101 | 1.0355 | 0.0138 | 15 |
| Lactic Light | 1.3113 | 0.0104 | 0.7211 | 0.0246 | 24.1 |
| acid Dark | 1.3113 | 0.0104 | 0.9935 | 0.0149 | 14.1 |
| Mustard Light | 1.3099 | 0.0148 | 0.8086 | 0.0274 | 25 |
| oil Dark | 1.3099 | 0.0148 | 1.1114 | 0.0187 | 13 |

When soil is used instead of sand as medium with the above substances as energy materials the efficiency of nitrogen fixation both in light and dark becomes much less as is evident from the following results :—

100 grams soil mixed with different amounts of energy materials.

Exposure for 4 months

| Substance | %C Initial | %N Initial | %C Final | %N Final | Efficiency |
|---------------|---------------|---------------|-------------|-------------|------------|
| Butter Light | 1.3548 | 0.0410 | 1.0752 | 0.0445 | 12.3 |
| „ Dark | 1.3548 | 0.0410 | 1.2072 | 0.0419 | 6.2 |
| Lactic Light | 1.3734 | 0.0411 | 0.9912 | 0.0453 | 10.9 |
| acid Dark | 1.3734 | 0.0411 | 1.1693 | 0.0423 | 5.9 |
| Mustard Light | 1.3374 | 0.0408 | 1.0518 | 0.0443 | 12.2 |
| oil Dark | 1.3374 | 0.0408 | 1.1786 | 0.0418 | 6.4 |

Exposure for 8 months

| | | | | | |
|---------------|--------|--------|--------|--------|------|
| Butter Light | 1.3548 | 0.0410 | 0.8213 | 0.0474 | 12 |
| „ Dark | 1.3548 | 0.0410 | 1.0810 | 0.0427 | 6.2 |
| Lactic Light | 1.3734 | 0.0411 | 0.6709 | 0.0486 | 10.7 |
| acid Dark | 1.3734 | 0.0411 | 0.9786 | 0.0434 | 5.8 |
| Mustard Light | 1.3374 | 0.0408 | 0.7933 | 0.0473 | 11.9 |
| oil Dark | 1.3374 | 0.0408 | 1.0034 | 0.0427 | 5.9 |

These results show that with sand which is more porous than soil the velocity of oxidation of organic matter both in light and dark is greater than in soil. Moreover, the total nitrogen content being smaller than in soil the efficiency of nitrogen fixation is greater in sand than in soil; a sandy soil can be more readily enriched from the nitrogen stand-point by the addition of organic matter than a clay soil, but the nitrogen fixed is lost more readily from sandy soils than from clay soils.

The foregoing experimental results show that when molasses which is readily soluble in water and rich in carbohydrates is added to the soil even after a month, the ammoniacal nitrogen, total nitrogen, Azotobacter numbers and total bacteria increase markedly both in light and in the dark. The nitrate nitrogen remains stationary at the beginning, then it increases. At no stage in the fixation of nitrogen on the addition of sugars, molasses, starch, glycerol etc., the sum of ammoniacal and nitric nitrogen, that is available nitrogen goes down in our soils although the total bacterial numbers go on increasing markedly. This behaviour is in marked contrast to the observations in temperate countries where sugars, when added to the soils, are known to reduce the nitric nitrogen content of soils. This is explained from the viewpoint that the sugars supply the energy requirement and cell materials for the multiplication of the bacteria, which absorb the available nitrogen from the soil for the formation of microbial proteins. It appears that in our soils the soluble carbohydrates are oxidized much more readily than in soils of temperate countries and in this process marked nitrogen fixation takes place both in light and in dark and the available nitrogen used up for the formation of microbial protein is more than compensated by the formation of available and total nitrogen due to the fixation of atmospheric nitrogen. The proteins formed in nitrogen fixation are also readily oxidized to available nitrogen in our soils. The available nitrogen and the sugars being readily soluble in water exist in the aqueous solutions and also partly adsorbed on the soil surface.

Decrease of available nitrogen with celluloses and fats although there is much of fixation.

On the other hand, although, there is nitrogen fixation by mixing lignin, celluloses and fats with soil as recorded above and the total nitrogen increases, there is no increase of ammoniacal or nitric nitrogen for a long time. It appears that the available soil nitrogen in these cases is partially taken up by the increased number of micro

organisms for their microbial protein. The velocity of the oxidation of cellulose, lignin and fats in the soil is much smaller than with soluble carbohydrates and hence the fixation of nitrogen and the formation of protein and available nitrogen with fats, lignins and celluloses are much smaller in an unit time than with soluble carbohydrates. Moreover, a part of the available nitrogen may also remain adsorbed not only on the soil surface but also on the unoxidised fat or cellulose or lignin which are insoluble in water. Hence in this latter case there is fall of available nitrogen, although there is increase of total nitrogen.

The foregoing observations are strongly supported by the recent experiments of S. Mattson and E. Koutler-Andersson (Ann. Agr. Col. Sweden **11**, 107-134, 1943) and E. Bennett (Soil Science 1949. **68**, 399) who have reported that ammonium hydroxide is strongly adsorbed by lignin and other organic substances when they are mixed with ammonium hydroxide and a current of oxygen is passed at 25° for 150 hours. The solution or suspension of lignin during the treatment became very dark. When complete methylation had preceded oxidation, lignin was insoluble and there was no change of colour. The ammoniacal nitrogen was 33% of the total nitrogen adsorbed. These workers have shown that a part of nitrogen adsorbed was resistant to the action of 72% sulphuric acid and strong alkaline solutions. A relatively high percentage of nitrogen added during oxidation remains bound even after drastic methylation. These results throw considerable light on the marked stability of the nitrogen compounds present in coals which are formed from cellulosic and lignin matter present in plant materials.

Nitrogen Fixation, humus Formation and residual effect of a manure.

A few years ago, in an article in "Nature" (Vol. 151, 338, 1943) I stated that the residual effect of a manure will depend on its power to fix atmospheric nitrogen. Such materials show residual or beneficial effect to a succeeding crop. This view point will be clear from the following considerations:—

When ammonium salts or nitrates are added to the soil, a better crop yield is obtained, but these materials hardly add any humus which requires both carbon and nitrogen. In such a case hardly any nitrogen is saved for the next crop. On the other hand, when urea, blood, rotten fish, wool residue, guano etc., which are nitrogen rich materials with a ratio of carbon/nitrogen less than 10, are added to the soil, fairly rapid nitrate formation takes place and the crop sown after a month or so, is benefitted. Due to the presence of a certain amount carbon in the compound an appreciable amount of humus, rich in fats, proteins and microbial cells, may be stored in the soil and a small residual effect may be observed in the succeeding crop, provided the time interval between the sowing of the crop and the addition of the manure is not large. If the time interval is large, the humus may be oxidised and the whole of the nitrogen may be lost. Similarly, leguminous green manures with a carbon/nitrogen ratio of 10 to 13 actually add a large amount of nitrogen to the soil, and if the acidity is not large, with a time interval of two or three months, a better crop may be produced.

But the residual effect in this case is not likely to last long. As a matter of fact, no practical farmer has reported any residual effect with substances like blood, urea, nor even in the case of composts. The Rothamsted results with green manure like clover show that the residual effect lasts for 3 to 4 years at most. On the other hand, with farmyard manure with a carbon/nitrogen ratio of 20 or more, the residual effect is more permanent.

In all our experiments with materials like molasses with a carbon/nitrogen ratio of about 40 or more, cow-dung (C/N ratio 20), neem leaf (C/N ratio 25), wheat straw (C/N ratio 65) etc., we have always obtained marked fixation of nitrogen and humus formation both in light and in dark. Since with these materials added to the soil not only the humus corresponding to the originally present nitrogen, but also an additional amount corresponding to the fixed nitrogen is added, it is clear that with these materials the total nitrogen and humus added to the soil always exceeds the nitrogen and humus

actually added in the manure. Specially in cold countries where the oxidation processes are slow and the carbon/nitrogen ratio of the starting materials is high, the fall of the carbon/nitrogen ratio in one year may not be much and the carbon/nitrogen ratio may not reach the value 10 to 1. Hence the fixation of nitrogen and formation of humus may continue even in the second or third year after the addition of carbonaceous compounds. Since the carbonaceous compounds act as a marked protein sparer in soil as in the animal body, the processes of ammonification, nitrification etc., of the protein matter are slowed down and losses of nitrogen will be reduced to a minimum due to the presence of the carbonaceous compounds. Therefore, in these cases subsequent crops will be benefitted even without the addition of any manure as is observed in the classical Rothamsted experiments and elsewhere.

In composting, the aim is to save the nitrogen present in the material and to add it to the soil with approximately ten times its weight of carbon along with minerals and microorganisms, that is, in the form of humus. But in most experiments with composting, there is loss of nitrogen in addition to its being tedious and troublesome, as observed by workers all over the world.

The only difficulty in the direct addition of plant materials is that a time interval is needed between the addition of the carbonaceous substances and the sowing of the crop. But with molasses at the rate of 10 tons per acre, a time interval of 5-6 weeks is quite adequate in our country. With cow-dung six weeks is adequate and with Neem leaf 6-7 weeks. But straw requires 10-12 weeks. In cold countries the period may be about double of that in tropical regions. If our aim is to draw one crop every year, the addition of carbonaceous substances like farmyard manure or green plant residues at the rate of 8-10 tons per acre should work with a time interval of about six months and should produce beneficial results even in temperate climates. If the time interval has to be minimised, a few pounds of urea, blood or inorganic nitrogenous manures per acre (say 20—25 lbs per acre) should prove effective.

It is interesting to note that stubble and roots that are left in the fields after harvesting supply the following amounts of carbon to the soil per acre in pounds :—

Oats (1877), wheat (1914), rye (1730), barley (2186), red clover (3833) and lucerne (4610).

It has been reported in the dry farming sections of Nebraska by Russel in 1929 that an increase in available nitrogen effected by a legume may increase crop growth but may cause the reduction of soil moisture. This accounts for the tendency of crops to "fire" when following alfalfa. On the other hand, the addition of cellulose rich materials may cause a deficiency of available nitrogen. A solution of the problems consists in supplementing the use of nonleguminous materials with suitable nitrogenous fertilizers.

Humus liberates nitrate more slowly than ammonium salts

Since 1920 we have shown that a substance which is capable of taking up oxygen can readily retard the oxidation of another substance when mixed with it. This is a perfectly general phenomenon and is applicable to reactions *in vitro*, in the animal body, in the plant as well as in the soil. More than fifty years ago physiologists observed the marked protein sparing capacity of carbohydrates in the animal body. In a number of papers we have shown that organic substances like molasses, sugars, cellulose containing materials like leaves, plant residues, fats etc. markedly retard the velocity of oxidation of proteins, urea, amino acids, ammonium salts etc., when added to the soil. In the rapid oxidation of nitrogenous compounds there is marked loss of nitrogen in the gaseous state due to the formation and decomposition of the unstable substance, ammonium nitrite, which is an intermediate product in the processes of ammonification and nitrification of nitrogenous compounds. Hence nitrogenous compounds when mixed with carbonaceous compounds, as in humus undergo slower oxidation and liberate ammonia and nitrate for a longer period for the benefit of the crop than in the absence of carbonaceous materials. Moreover, in the slow liberation of nitrates, the danger of leaching is less. The

foregoing considerations clearly explain why ammonium salts or nitrates do not improve the nitrogen status of soils but organic manures can do so and that the nitrogen content can increase permanently only when the nitrogenous compounds are associated with carbon compounds.

From times immemorial, people have used organic compounds farmyard manure, leaves, vegetable residues in manure heaps because of their nitrogen contents. We were the first to emphasise that the greater the carbon /nitrogen ratio of such manures the greater is the nitrogen fixation and humus formation when mixed with soil.

Humus in which the carbon/nitrogen ratio is 10 or more can liberate ammonia and nitrate for a longer period and more slowly than the same amount of nitrogenous compound added to soil without carbonaceous compounds.

Even to-day, crop production is caused chiefly by the nitrogen of the humus present in all soils, as only 3 % of the world crop production has been attributed to artificial manures. In soils of cold countries the humus nitrogen is usually 2500—3000 lbs. per acre in the first 9" of the soil and out of this 1—2%, *i.e.*, 25—50 lbs. is in the form of ammonium salts and nitrates, *i.e.*, available nitrogen. If to this soil 20 lbs. of nitrogen in the form of ammonium sulphate or nitrate are added, beneficial effect to the crop growth is expected. On the other hand, in tropical countries the total nitrogen content in the soil is of the order of 1000—1200 lbs. per acre in the first 9". But usually the available nitrogen is 10 % or more in such soils. Hence the available nitrogen in tropical soils is nearly 100 lbs. per acre. It appears that the addition of 20 lbs. of nitrogen from artificials cannot be as effective as in temperate climates where the available nitrogen already present in the soil is less. The aim of scientific and constructive agriculture specially in tropics should be to increase the humus capital which readily gives out available nitrogen and minerals required for crop growth slowly without less danger of leaching than with artificial manures.

In forest soils all over the world the humus is greater than in arable mineral soils. But the liberation of ammonia and its oxidation to nitrate is controlled by (a) pH of the soil (b) the temperature and (c) the solar light. In acid forest soils the carbon/nitrogen ratio is much greater than 10 and hence the total nitrogen content and its availability is usually not high.

Acid soils have larger and alkali soils smaller carbon/nitrogen ratios than normal soils

The carbon/nitrogen ratio in certain forms of humus has been a puzzling phenomenon. From a study of data obtained by various workers, the conclusion was reached that the carbon/nitrogen ratio tends to become narrower as the age of the humus increases.

Studies by previous workers on the influence of soil treatment upon the ratio of humus decomposition, as measured by carbon dioxide evolution show that the carbon oxidation slows down as the pH is more on the acidic side. This was also shown by Dhar and Pant in "Nature" (1942, 149, 84).

When humus has a wide carbon/nitrogen ratio, as in the case in soils shortly after receiving large applications of plant materials or little decomposed manure or in the 'F' layer of raw humus forest soils, there is still considerably greater liberation of carbon as carbon dioxide than of nitrogen as ammonia, with the result that the carbon/nitrogen ratio of the humus tends to become narrower. When the initial ratio was 17.9—1, no nitrate was produced in a sand culture. However, when the carbon/nitrogen ratio of the humus was 13.1—1, considerable nitrate was formed.

Work on mull soils has indicated that acids decrease the carbon oxidation and ammonia oxidation markedly. We have been reporting for a number of years that the greater the average temperature of the soil, the greater is the pH of the soil. This is certainly due to the fact that organic matter of the plant residues added to the soil in tropical countries is quickly oxidised leaving small amounts of humus and chiefly minerals in the soil. Thus, the pH of soils in Egypt and India

is greater than in soils of cold countries. This is a sort of auto-catalytic effect, as alkalis help oxidation of carbohydrates readily. On the other hand, in acid soils as in cold countries, for increasing oxidation, lime or calcium carbonate has been recommended.

In composting in Indore it has been found that the pH increases as the composting progresses and when the composting finishes, the pH is of the order of 7.3—7.4. It is interesting to note that as the pH goes to the alkaline side the total nitrogen in humus also increases.

Percentage of nitrogen in humus of tropical soils is greater than in temperate climates

This raises a very important issue. Although the total nitrogen in tropical soils is low, the percentage of nitrogen is higher than in humus of cold countries which are on the acidic side. It is clear, therefore, that manuring by carbohydrates and cellulosic materials for increasing the nitrogen status of a soil is certainly more profitable in tropical or semi-tropical countries than in cold countries, not only because the velocity of oxidation of carbohydrate materials is slower in cold countries and hence the nitrogen fixation is less pronounced, but the nitrogen fixed will be converted into ammonia and may not be available to the crop because of the lack of nitrate formation. In cold countries it has been repeatedly observed that the improvement of the nitrogen status of a soil depends on the calcium status as has been markedly emphasized by Hudig in Holland.

If a large dose of lime or calcium carbonate is added, the excess reacts with the ammonium salts and proteins with loss of nitrogen. S. K. Mukerji and N. R. Dhar observed that when large quantities of calcium carbonate are mixed with molasses and soil, the efficiency of nitrogen fixation is less than in presence of small doses of calcium carbonate. E. V. Seshacharyulu and N. R. Dhar found that the efficiency of nitrogen fixation with 2% carbohydrate and soil in presence of calcium carbonate is less than in its absence. Similarly M. C. Pant, H. L. Nigam and N. R. Dhar showed that in the study

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of the loss of nitrogen in the nitrification of ammonium salts, the smell of ammonia is obtained when 1 or 2 gms. of calcium carbonate are added to 100 c.c. of ammonium salt solution and the loss of nitrogen is less with 1 gm of calcium carbonate. It is clear, therefore, that although calcium carbonate and other salts help in the coagulation of impervious soils, an overdose produces loss of fertility due to the loss of ammonia and nitrogen in the gaseous state.

S. C. Sen under my direction has worked with a very large number of soils collected from different parts of Bihar. His results show that when the pH values of alkaline soils varies from 9.2 to 8.6, the carbon/nitrogen ratio may have the low values 2.86, 3.41, 3.38, 4.15 etc. Sen has shown that soils collected from Ranchi (Bihar), which is 3000 ft. above sea-level, have pH values ranging from 4.4 to 5.2 and the carbon/nitrogen ratio varies from 11.4 to 20.3. A soil sample from Coonoor (Southern India) which is above 6000 ft. showed a pH value of 4.8 and carbon/nitrogen ratio of 11.6, the total carbon being 1.72% and nitrogen 0.148%.

In a recent article (Dhar and Pant : "Nature" 1942, **149**, 48) it was concluded from the experimental results obtained with soils of different countries that acid soils have higher carbon/nitrogen ratio and alkali soils smaller carbon/nitrogen ratios than surface neutral soils.

This conclusion regarding acid soils has been supported by recent work. Evans and Rost obtained the following results with Minnesota soils :—

- | | |
|--------------------------------------|---------------------|
| (1) Chernozems | ; pH—6.3 ; C/N—11.4 |
| (2) Black prairie soils | ; pH—5.4 ; C/N—11.8 |
| (3) Podzols of North Central Regions | ; pH—5.4 ; C/N—11.8 |
| (4) Podzols of North Eastern Regions | ; pH—4.6 ; C/N—15.1 |

Moreover, Nair (M. Sc. degree thesis, Travancore University 1945) working with black 'Kari' soils of Travancore occurring in

coastal plains alongside some of the back waters and adjoining the Arabian sea obtained the following results :—

pH—6.7 ; C/N—11.1

pH—5.1 ; C/N—16.2

pH—4.5 ; C/N—26.2

pH—4.7 ; C/N—27.2

pH—3.9 ; C/N—30.1

Hence, the higher the acidity of the soil, the greater the carbon nitrogen ratio, i.e., the smaller the nitrogen content of the soil.

Peat, lignite and other varieties of coal containing humus as manures.

As peat, lignite and other varieties of coal are believed to be formed chiefly from plant materials which have been used by us for manuring fields, the former materials should serve as manures also.

The typical analysis of humic acids prepared from humic coal is carbon 60.5%, hydrogen 3.34%, nitrogen 2.03%, sulphur 1.44% and ash 1.96%. The nitrogen content of humic acid is due to the presence of protein associated with them. Some of the nitrogen in the humic acid molecule is considered to be bound cyclically, the nitrogen having replaced a heterocyclic oxygen atom.

By the extraction of soil humus, humic acid preparations and peat, substances have been obtained which prove quite definitely the protein nature of nitrogen in the younger fossils.

C. A. Weber defined peat as follows :—

“Peat is an organic mineral formed out of dead cellulose-rich plants by special process of decomposition. It is soft in its natural moist condition and is very rich in water. Peat contains largely the elements, carbon, hydrogen, oxygen and in addition varying amounts of nitrogen, sulphur and ash”.

Humus in peat, lignite and coals.

All the peats are rich in lignin-like complexes. It is generally assumed that nearly all the nitrogen in peat is in an organic form and

is not readily acted upon by micro-organisms in the undrained peat but is acted upon very slowly when conditions are made aerobic as by draining.

In addition to cellulose and pentosans various peats contain also hemi-cellulose and hence mannose, galactose, levulose and other pentoses are formed on hydrolysis of peat with dilute hydrochloric acid. The carbohydrates present in peat when mixed with soil and allowed to oxidize partially cause nitrogen fixation.

During the formation of peat the woody matter becomes more or less disintegrated and the structure of the material both physical and chemical is greatly altered. This process is chiefly biochemical, the major part of the disintegration being brought about by the action of micro-organisms and fungi. The biochemical process may cease with only partial decomposition of the woody texture, leaving the peat in such condition that lignite or woody coals are formed later.

The second stage in the formation of coal is brought about by dynamo-chemical processes which greatly alter the physical and chemical properties of the hydrated peat formed during the biochemical decay. A further step is brought about by the application of intense pressure often resulting from an upward thrust of the earth's crust causing a further loss of water accompanied by liberation of carbon dioxide, carbon monoxide and other gases. The coal decreases in volume and is cemented together depending upon the temperature and pressure conditions thus yielding the different types of coals.

Nitrogenous compounds in coal

In the coalification process nitrogen originally present as amino or amido groups is converted to some other non-basic form which is not extracted by mineral acids. The nitrogen from younger fuels is removeable by mineral acids. It is believed that during coalification the reactive amino and imino groups which are present in the younger fuels are involved in reactions with other groups such as carboxyl, hydroxyl, carbonyl and methoxyl which convert the basic groups

into non basic groups, the nitrogen being held in a heterocyclic or else linearly linked between units of such complexity and negativity that the nitrogen loses its basic properties.

Evidence indicates that a large part of nitrogen in humic acid is also bound cyclically. From studies of solvent extraction, vacuum distillation, combustion, oxidation, hydrogenation, halogenation and hydrolysis of coals of various ranks, the nitrogen in coal can be pictured as being present mostly in a hetero-cyclic linkage.

It is well known that lignin is the material which resists oxidation much more than other carbohydrates. Even lignin when mixed with soil undergoes oxidation. Peat which is rich in lignin-like complexes fixes nitrogen and reclaims alkali soil. Similarly lignite and brown coal should be effective for both the purposes. Bituminous and anthracite coal should be less reactive. Very finely powdered coals of all types should be able to supply nitrates to the soil by slow oxidation of the hetero-cyclic and other nitrogenous compounds and also fix the nitrogen of air. This must occur much more so with peat, dopplerite and brown coal rather than with anthracite coal. In our recent experiments carried on with peat, brown coal (lignite) and bituminous coal in a finely divided condition mixed with soil, nitrogen fixation is observed more in light than in dark. We have also observed a marked beneficial effect of these materials on crop production with normal soils and in the reclamation of alkali soils.

It is believed that in composts about 8—10 % of the total nitrogen is in the available form and hence compost is a quick acting manure in comparison with coal, which is certainly more ancient and inert than the humus in most soils. But if the coal is very finely powdered and mixed well with the soil, it not only should impart its nitrogen to the soil gradually but should be able to fix atmospheric nitrogen in the process of its slow oxidation to carbon dioxide and this has actually been observed by us with bituminous coal and lignite. Coal is certainly cellulosic or lignin substances mixed with protein of animal

and plant sources with some decomposition products from fats, barks, waxes, resins but the reactive groups like carbonyl, carboxyl, hydroxyl, methoxyl and amino group seem to have been removed by the influx of time because chemical changes have taken place intramolecularly or by the interaction between proteins and the cellulose and the lignins. Although coal appears to be rather dead matter in comparison with compost or humus of soil but there is a redeeming feature in coal which is this : coal adds large quantities of carbonaceous substances which are less reactive than the carbonaceous substances present in plant residues. And hence on the addition of coal to a soil, the available soil nitrogen is not likely to be converted into microbial cells as happens when cellulose, lignin or fat is added to the soil. Microbial cells may not use all the available nitrogen in soils but some part of the available nitrogen may form chemical compounds or adsorption compounds with cellulose, fats or lignins and would not be available to the growing plants. Coal, dopplerite, peat or brown coal being more inert than fresh plant materials will not be reacted upon by microorganisms quickly but should definitely help aeration and perhaps increased water retention capacity of the soil. If one ton of coal containing 2% nitrogen and about 75 % carbon is added to the soil in a finely divided condition, the following results are obtained :—

- (a) 44 lbs of total nitrogen will be added and this nitrogen may be available in 2 or 3 years ; (b) 1640 lbs of finely divided carbon will be added per acre and about 1200 lbs may be oxidised in about 2 or 3 years and this may lead to a fixation of about 30 lbs of nitrogen which will be utilised by crops. It appears, therefore, that coal should prove to be a moderately good nitrogenous manure specially to tropical soils when either added in a very fine state of division alone or mixed with molasses or cowdung or plant leaf, the younger varieties like peat, dopplerite, brown coal should yield better results than anthracite. There is no doubt that

coals are colloidal substances containing colloidal carbon peptized by large quantities of hydrocarbon like compounds consisting of partially deoxidised celluloses, lignins and small quantities of proteins. It seems that a part of proteins has passed into other stabler forms of nitrogenous substances.

As alkalis help oxidation, the oxidation of cellulose and lignin and coal when added to the soil will be more easy in tropical soils which have a tendency to be alkaline than in soils of temperate countries which are acidic. It is clear, therefore, that the foregoing considerations are more applicable to our soils than in cold countries where liming has to be taken recourse to if carbohydrate or coal manuring has to be adopted. With adequate amounts of lime or chalk and coal extremely well pulverised, moderately good results should be obtained specially with peat and lignite and bituminous coal which are abundantly present in European and cold countries. When mixed with calcium carbonate they should not only improve the calcium status but should also improve the nitrogen status of soils. When this mixture of peat and calcium carbonate or coal and calcium carbonate is very well mixed with soil by deep cultivation and aeration of soil which will be aided by the large surface introduced in the form of finely divided coal or peat, crop production should be improved.

The chief differences between composts or humus of the soil and coal are as follows :

- (1) Coal is definitely more aged than compost.
- (2) The carbon/nitrogen ratio of coals, even the younger ones, is greater than that in composts although acidic composts or humus or composts present under acid soil conditions have much larger carbon/nitrogen ratio than those prepared in neutral or alkaline conditions.
- (3) The nitrogen present in coal is not chiefly in the protein condition as in composts.

- (4) The number of micro-organisms in a definite weight is certainly larger in compost than in coal.
- (5) The water retention capacity is less in anthracite and bituminous coal than in composts.
- (5) The inertness of the organic ingredients in coal is greater than in composts.

These factors may be the chief reasons why coal is considered to be a stone and dead matter in comparison with plant residues, or humus present in the soil. Is there any other important criterion differentiating dead and living matter? Is it possible to revive coal after mixing it with plant leaf, cowdung or sugar or agar or any surface-active substance?

It is generally believed that the oxidisability of the products of photo-synthesis in the plant tissues decreases with the increase in the molecular weight or complexity of the molecules. The order seems to be as follows :—

Formaldehyde—glucose—canesugar—starch—cellulose—lignin. The case of protein synthesised in the plant kingdom is more complicated. Our experimental results show that amino acids like glycine, aspartic acid etc. are synthesised in the plant kingdom or *in vitro* by the action of nitrates on glycol, sugars, glycerol, organic acids etc. either by absorption of oxidation energy or solar energy or both aided by titania. These amino acids undergo polymerisation and condensation and form proteins.

In carbohydrate synthesis, starch is readily detected when plant leaf free from carbohydrate is exposed to light and that is why Sachs concluded that starch is the first product in photosynthesis. In our experiments in photo-oxidation of various carbohydrates, Palit and Dhar observed that the oxidation of starch is slightly greater than other soluble carbohydrates. In our recent experiments on the induced and photo-chemical oxidation of cellulose and lignin carried on by Dinesh Pant and Dhar, it is observed that both the substances

can be oxidised very slowly by air at the ordinary temperature. The oxidation of starch is very much greater than either that of cellulose or lignin. There is no doubt that in nature, both cellulose and lignin, are oxidised but much less readily than starch or sugars. It has been established in recent years that when plant materials are allowed to be oxidised in the soil, the soluble carbohydrates disappear first, then cellulose, finally lignin, which disappears with great difficulty. This is the position in aerobic condition where oxidation can take place with the help of micro-organisms and the presence of surface and light. In anaerobic condition it is believed that the same order of stability is also observed but the speed of disappearance of organic substances is smaller and acids are produced in the first stage.

It is of interest to record here that in a recent paper Spoehr and Milner (Plant Physiology 1949, 24, 120) have described a method for determining the degree of reduction of the total organic matter of plant material from its elementary chemical composition. The degree of reduction is believed to be proportional to the heat of combustion and is an expression of the energy content of the material. With proteins condensation with lapse of time, goes on. The formation of skin, hide, hoof, horn etc. is a manifestation of polymerisation and condensation and these materials resist oxidation well. Similarly carbohydrate and celluloses and tanning materials can form barks of trees which also resist oxidation. It is clear, therefore, that when plant materials containing carbohydrates, pentosans, starch, cellulose, ligno-cellulose, lignin, bark, fats, resins, waxes, simple and complex proteins, are mixed with large amounts of soil, they undergo slow oxidation through the agencies of bacteria, fungi, chemical surfaces, catalysts, light etc. but the velocity of oxidation differs greatly depending on the nature of the material undergoing oxidation. The waxes, resins, barks etc. seem to resist oxidation more vigorously than even fats and lignins. Similarly the complex proteins also are stable. Moreover by the combination of some of the proteins and the lignin or cellulose or bark, humus like chemical compounds or adsorption compounds may be formed and these

not only supply ammonia and nitrate slowly but can give up potash, phosphate and other mineral matters slowly to the soil.

On the other hand, under anaerobic conditions, i.e., when coals are formed in nature the position may be as follows :—

Instead of carbon dioxide, as in the case of aerobic oxidation, methane, hydrogen, carbon monoxide are formed along with acidic substances. Frequently it has been observed that the acidity of the products of decomposition and oxidation is greater in anaerobic than in aerobic conditions. It is well known that the velocity of oxidation of carbohydrates decreases as the acidity of the system increases. Consequently the disappearance of plant materials is quicker in aerobic than in anaerobic conditions. The acids produced in both aerobic and anaerobic conditions, more in latter than in former, act as preserver of the carbohydrate, lignin and cellulosic materials whilst they may help the decomposition and oxidation of protein substances to the ammonia stage and a part of the ammonia may be washed out. Hence it has always been observed that the carbon/nitrogen ratio of organic substances in soils is greater in acid media than in neutral or alkaline condition. In the virgin prairies and steppes rich in humus, the carbon/nitrogen ratio has generally been observed to be greater than 10 and these soils are acidic. After cultivation, the acidity falls off because of the oxidation of acidic substances and there is a fall in carbon/nitrogen ratio. Similarly the carbon/nitrogen ratio of the organic matter in peat, dopplerite, etc. is of the order of 30 or more and these materials are distinctly acidic. It is well known that most of the coals are also acidic and the carbon/nitrogen ratio of the coals may vary from 120 to 30 depending on the conditions of coalification. It is generally accepted that the carbon/nitrogen ratio of the wood from which coal is obtained is greater than that of the coal; in other words, the percentage of nitrogen in wood is smaller than that of coal.

In the Indore method of composting under aerobic conditions with carbon/nitrogen ratio of starting materials varying from 130

to 20 the compost formed has a carbon/nitrogen ratio ranging from 17 to 12 and pH 7.2 to 7.4. If such plant materials are composted in anaerobic conditions, the carbon/nitrogen ratio of the material formed is likely to be larger due to acidic conditions. In the Indore method of composting the temperature of the heaps may go upto 80°; this not only kills the micro-organisms and the weed seeds but also help in the liberation of carbon or charcoal or graphite like substances.

Carbon and nitrogen contents of coal.

In coal formation water is believed to play as important a part as high temperature and pressure. Water freed from oxygen helps making the conditions in peat formation practically anaerobic and also help in the washing away of ammonia and other soluble compounds formed in the processes which consist of auto-oxidation and reduction, hydrolysis and decomposition, polymerisation etc., specially under high pressure. It is generally believed that plant, animal and micro-organic substances when covered with shallow water lead to peat formation which is the first step in coalification. In this process dehydration and formation of black substances resembling charcoal or graphite in small quantities, takes place. The material produced has a marked tendency to adsorb moisture because of its colloidal nature. Peat or dopplerite perhaps resembles the black material obtained by the action of strong sulphuric acid on cane sugar. This material swells and forms a jelly readily although it does not contain any nitrogen, it may be considered to be something like humic acid. If protein substances are present or added to it, unstable chemical compounds between protein and this jelly are likely to be formed as investigated by Page and co-workers (*J. Agric Science*, 1930, **20**, 460). It seems that in the coalification process the starting material may be peat or dopplerite, which chiefly consists of humic materials or the "fundamental jelly" as stated by coal specialists. This jelly like substance in course of time loses its activity and water retention capacity and chemical reactivity. Moreover, the protein matter originally present either as adsorption or chemical compound may be liberated due to the decrease of chemical affinity of the humic matter

and may undergo decomposition or hydrolysis or auto oxidation and reduction. In this process the carbon content increases and nitrogen status decreases chiefly due to the liberation of ammonia and its removal. This is supported by the fact that as the rank of the coal increases generally the carbon increases and nitrogen decreases, specially in anthracite coals which are the most ancient. This is clear from the following table which shows the relative composition on an ash-free and moisture-free basis :—

| | <i>Total carbon.</i> | <i>Total nitrogen</i> |
|----------------------|----------------------|-----------------------|
| —Wood | 49–50 % | 1.1 % |
| Peat | 56–57 % | 2.95 % |
| Lignite .. | 72–79 % | 0.98 % |
| Sub-bituminous | 76 % | 1.47 % |
| Bituminous | 87 % | 1.37 % |
| Semi-bituminous ... | 89.1 % | 1.40 % |
| Semi-Anthracite ... | 92.1 % | 1.20 % |
| Anthracite | 94.4 % | 0.71 % |

Moreover , in coalification from peat or plant materials high temperature and pressure play a very important role and this helps in the carbonisation or formation of more charcoal or graphite like substances or perhaps the partial decomposition and stabilisation of the undecomposed nitrogenous substances. There is no doubt that the percentage of carbonaceous or graphite like matter is greatest in anthracite and least in peat or dopplerite, which is more allied to the initial plant or animal material or both than anthracite or bituminous coal.

In the high ranking coals the carbon chiefly exists as charcoal or graphite like substances and the nitrogen as nitrides, amides and in the hetero-cyclic condition and both the carbonaceous and nitrogenous substances can resist oxidation more markedly than those pre-

sent in peat or dōpplerite. It is well known that plant residues, i.e. leaves, stems, roots, straw etc. not only add a part of the carbon and practically the whole of the nitrogen, they contain to the soil and can also manure the land by fixation of nitrogen by the partial oxidation of carbonaceous substances aided by light. Similarly the humus formed from plant residues either in the soil or compost heaps is certainly not as aged and as rich in charcoal or graphite like substances as anthracite coal. Consequently the humus which undergoes a slower oxidation in the soil than the original plant material is more readily oxidised when mixed with soil than anthracite or bituminous coal. It is clear, therefore, that the manurial value of the soil humus is quicker than that of anthracite or bituminous coal. It seems that the instability of a manure when mixed with soil and the speed of liberation of ammonia and nitrate will depend on the presence of chemical compounds resembling carbohydrates and celluloses, which are known to oxidise and liberate energy readily. On the other hand, when the manure is rich in charcoal or graphite like substances, which are more inert than carbohydrates, they are not likely to undergo ready oxidation in the soil.

Soot as a manure.

In this connection, it is interesting to note that soot obtained from domestic fires and industrial uses of coal is used by farmers as manure. The value depends partly on its physical effects on the soil and partly on its contents of nitrogenous and sulphur compounds. It is largely used as a top dressing for wheat in the early months of the year. The dead black colour of soot makes it a good absorbent of solar radiation so that the soil which has been treated with it is kept warmer than untreated land, whilst the nitrogenous compounds present in soot are valuable fertilizers. The carbon and nitrogen contents of coal and the soot obtained from it are as follows :—

| | Carbon % | Nitrogen % |
|------------|----------|------------|
| Soot | 40.5 | 4.1 |
| Coal..... | 69.3 | 1.4 |

It has been reported that peat fires are kept burning all day and most of the night in the thatched houses and the only exit for the smoke is the doorway in the houses in the Hebrides. The thatch containing the soot is applied to the land for fertilization. The thatch is renewed annually. In the Hebrides, cows are housed under the same roof with the human beings and the cow manure is removed once a year and added directly to the land.

Molasses, soluble carbohydrates and glycerol when added to the soil are oxidised quickly and fix nitrogen and enrich the soil and can behave as quick acting, nitrogenous manures specially in tropical countries. On the other hand, when materials rich in cellulose, lignin and bark are added to the soil, the oxidation of the organic matter is much slower than in the previous case. Fats, resins, waxes also resemble the latter class. The case of mobil oil is peculiar. Although it is rich in carbon and hydrogen and is free from oxygen, it undergoes oxidation in the soil with very great difficulty and hence is not suitable as a quick acting nitrogen fixing material but these substances may increase the aeration and porosity of the soil. Saw-dust rich in lignin and lignino-cellulose behaves in the same way and markedly resists oxidation when mixed with soil. Charcoal or graphite when mixed with soil may increase the porosity and aeration but may not be able to fix nitrogen.

With protein substances, when mixed with soil, the simpler the constitution of the protein, the greater is its power to behave as a quick acting manure. Amino acids when added to the soil undergo ammonification and nitrification readily. Similarly human excreta containing amino acids and proteins, rotten fish etc. can behave as quick acting manures. Blood, oil-cake etc. containing fats do not undergo oxidation in the soils so readily and may not behave as very quick acting nitrogenous manure as the previous group. Hoofs, horns, hides etc. are formed as highly polymerised proteins of large molecular weight and when mixed with soil undergo very slow oxidation to ammonia and are not likely to act as quick acting manures. These complex protein matters are likely to remain in the soil for

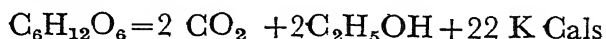
long periods and may behave as slow reacting nitrogenous substances.

That the decomposition of pentosans decreases rapidly and the total carbon increases with the depth of peat indicate how quickly the original cellulose and other plant materials are transformed into humic products. Moreover the original woody structure is well preserved in some lignites and that is why the lignite or brown coal should be more valuable as manure than anthracite coal.

Coal formation from plants.

It is clear from the existing literature that coal is formed under more anaerobic than aerobic conditions and coals are usually acidic. Consequently, the carbon nitrogen ratio of all samples of coal varies from 30 under the most favourable conditions to about 100 or more. The young varieties of coal like peat, dopplerite are acidic. Coals which are rich in sulphur should prove good manures for alkali soils.

In the process of coalification as in the sequence, wood (lignin and cellulose) → peat → brown coal (lignite) → bituminous coal → anthracite coal → graphite → diamond, there is not only dehydration or loss of water but there is also loss of oxygen over and above the loss of oxygen as water. In other words, auto-oxidation, and reductions involving the production of carbon dioxide and perhaps carbon monoxide and organic acids take place along with the reduction of the cellulose or lignin or sugar. It is well known that glucose in presence of yeast undergoes the following change :—



The alcohol is more reduced than sugar and the carbon dioxide is more oxidised than sugar. Hence this is a process of auto-oxidation and reduction. The alcohol on dehydration may be converted into ethylene. Similarly the cellulose or lignin molecule in forming peat or coal must be partially converted into carbon dioxide and perhaps carbon monoxide and organic acids and alcohols which on dehydration may yield hydrocarbons. The complex hydrocarbons may in turn break up into carbon and hydrogen.

Colloidal carbon in humus and coal

The black material obtained in composting straw, plant residues, the black substance obtained in drains and in underground sewers and perhaps the black mass obtained by the action of concentrated sulphuric acid on sugars, filter paper, straw, saw-dust and the black material in soil humus as well as that of coal, may be identical. Moreover, in composting thin layers of straw, though the temperature does not exceed 40° and there is a lack of high pressure, black masses are obtained. The mechanism of this blackening process is not very clear. In coal formation the temperature may go upto 100° or more and pressure may be high; but in peat formation which takes place under water, neither the pressure nor the temperature can be high. There is no doubt that cellulose, lignin and proteins take part in peat formation. As petroleum is also derived from vegetable and animal residues, it may be that hydrocarbons play a part both in coal and petroleum formation.

It seems that lignin can form woody coal but the cellulose, pectin and perhaps the sugars derived from pectin and cellulose may form jelly like substance or the 'fundamental jelly' of the coal scientists. This idea is supported by the fact that the black substance formed by the reaction of sulphuric acid on straw or cane sugar sets to a jelly readily. From the literature on the formation of coal, it is clear that apart from the mineral matter, carbohydrate, proteins, fats and waxes etc. of the vegetable world may form two important groups of compounds, one being the woody matter and the other, the jelly. The jelly may be the chief source of the volatile compounds in coal and the woody matter, the chief source of cokes, the protein matter might have been incorporated in the jelly.

A part of the oxygen of the cellulose is lost as carbon dioxide and this is oxidation and the alcohol formed as the reduction product by partial dehydration can form a hydrocarbon. Hence the coal substance may be a mixture or a solid solution of colloidal carbon, a hydrocarbon and an alcohol. Consequently, the oxygen loss of cellulose or lignin may consist of two causes. Firstly, loss of carbon

dioxide and possibly carbon monoxide, and loss due to dehydration of alcohol forming a hydrocarbon which can break up into carbon and hydrogen gas. This explains the ease with which, hydrocarbons, hydrogen, carbon monoxide etc. are given out on heating coal and its conversion into coke. Perhaps this mechanism of coalification throws light on the production of petrol in nature and also its production synthetically.

In our experiments with leaves, filter paper, saw-dust, cotton-wool, covered with water, both in light and darkness, even after one month, acids are obtained in aqueous solutions and there is appreciable blackening after three months, although the temperature never exceeded 40°. Cowdung is not acidic at all under these conditions.

With regard to the blackening under anaerobic conditions, a change takes place by which the organic matter is blackened, but the mechanism seems to be connected with some type of dehydration perhaps of the cellulosic material which forms the greater bulk of plant residues.

The decomposition of the bacteria, fungi, algae etc. which are present and active in the first stages of peat formation from vegetable and animal matter covered with water may produce black mass probably due to the liberation of carbon in the colloidal state. Similarly in composts and in the organic matters in drains, colloidal carbon may be formed by the partial decomposition of micro organisms.

Highly organised plants contain much less nitrogen than less organised plants. The nitrogen content of beech is 0.09 %, birch 0.10%, fir 0.05%, spruce 0.04%. On the other hand, bacteria contain up to 13 % nitrogen, algae 3.2 to 4.8, leaf moss 2.4 to 3.2 %, fern 1.6 to 2.4%, grass 1.6 to 2.4 % and swamp plants 1.6 %.

E. Terres (Proc. 3rd Intern conf. Bituminous coal, **2**, 797 (1931)) prepared artificial brown coals containing 4.16 % nitrogen by heating under pressure, peat moss containing 1.73% nitrogen after its

fermentation. The greater nitrogenous content of bituminous coal in comparison with brown coal or lignite has been ascribed to the existence of animal matter along with plant residues. Chlorophyll which is always associated with green plants, contains nitrogen and can add stable heterocyclic nitrogen containing molecules to coal. Chlorophyll and other porphyrins have been detected in coal. Protein materials such as chitins present in the coating of bacteria, in fungi cells, insects etc. may add nitrogenous substances to coal.

It is generally believed that most of the nitrogen present in humus is protein. The microorganisms which attack proteins in soils contain from 3 to 10% nitrogen. The plant residues usually added to the soil contain 0.32 to 2.4% nitrogen whilst the nitrogen content of soil humus varies from 1.3 to 5.6% showing an enrichment of protein in humus of the soil as a result of carbohydrate decomposition. Microbiologists postulate that the major source of protein in humus is the microbial body cells.

Carbon/nitrogen ratio of coal

The carbon/nitrogen ratio of peats varies from 30.8 to 40. With brown lignite the carbon/nitrogen ratio varies from 30.9 to 127. A sample of lignite containing more sulphur, that is, an acidic coal, showed a carbon/nitrogen ratio of 211. The black lignites have carbon/nitrogen ratios varying from 16.6 to 92. The semi-bituminous coals possess carbon/nitrogen ratios varying from 43.2 to 80 whilst sub-bituminous coals have carbon/nitrogen ratios ranging from 64 to 148. Bituminous coals have carbon/nitrogen ratios varying from 37 to 78, whilst anthracite coals show a carbon/nitrogen ratio, in most cases, of 100 or more.

It is well-known that soot is richer in nitrogen than coal from which it is derived and many samples of domestic soot have carbon/nitrogen ratios as in humus of soils, that is, approximately, 10, and soot collected from kitchen chimneys shows carbon/nitrogen ratio of about 13. The carbon/nitrogen ratio of low moor-peat is about 15.

We are trying to establish that all materials which burn or can be oxidised are capable of being used as agents for nitrogen fixation in soils or other solid surfaces. Composts as prepared at present burn readily and they supply nitrogenous matter to the soil.

Is coal or petrol or mobil oil an inert matter ? They burn readily in air but seem to be oxidised at the ordinary temperature on the soil surface with difficulty, and that is why the nitrogen fixation is a slow process.

Are death and dehydration connected phenomena ? Glucose, cane sugar, starch, cellulose and lignin, formed in the plants, are less and less hydrated as the molecular weight increases. Moreover, the nitrogen content of the plants decreases with increase of lignin, i.e., ageing.

Both animal and plant materials can be used as nitrogenous manures in the soil. A tree is a living thing, so are fungi, algae, bacteria, protozoa etc. They are rich in nitrogen and can serve directly as nitrogenous manure when decomposed in the soil as blood or other protein materials with carbon/nitrogen ratio smaller than 10. On the other hand, plant materials have carbon/nitrogen ratio greater than 10 and hence they not only add the small amount of nitrogen they contain but can fix atmospheric nitrogen and add humus to the soil.

The legumes are an interesting group, because they are both plant and bacterial products and hence, perhaps, intermediate between ordinary plant materials and bacteria. Their carbon/nitrogen ratio varies from 10 to 13 or more according to maturity and the amount of nodules present at the roots. They fix very little nitrogen even when mixed with soils and they have small residual effect. Plant materials with carbon/nitrogen ratio greater than 20 can fix nitrogen and increase humus for more than one year and hence possess residual effect longer in the soil than legumes.

Coal and petrol are certainly mixtures of vegetable and animal matters of which the decay is partially or completely stopped. It

is stated in Waksman's "Humus" that peat contains carbohydrates. We have observed that all carbohydrates can fix atmospheric nitrogen and increase humus, and hence the carbohydrate in peat should be able to fix nitrogen in soil. On the other hand, the carbon and hydrogen of the anthracite coal may be very inert at the ordinary temperature towards atmospheric oxidation and may not be able to fix nitrogen easily. Is it possible to measure the inertness of a combustible matter by its inability to fix nitrogen? There is no doubt that anthracite coal is less hydrated and contains smaller amounts of oxygen and nitrogen than coals of other ranks.

The urea-formaldehyde polymers when added to the soil may behave as moderately quick acting manures and will be certainly less quick acting than urea because of the presence of the carbonaceous substances derived from formaldehyde. If the nitrogenous substance has to remain in the soil for more than 2-3 months, urea-formaldehyde polymers should behave better than urea or ammonium sulphate alone. In case of sodium or potassium nitrates there is not only leaching more than in ammonium sulphate, but in our soil which has already a tendency towards the alkaline side, more alkalinity is produced and may not be, therefore, suitable for our soils.

Sir John Russell has reported that Hartley and Greenwood, (Emp. J. Expt. Agric 1933, **1**, 113) using one ton of farmyard manure per acre, obtained beneficial results very much better than an equivalent mixture of artificial manure in Nigeria. Moreover, Tempany and co-workers (Emp. J. Experimental Agriculture 1949, **17**, 145) have observed that ammonium sulphate renders no good to crops in stations in Malaya having 85" rainfall; but farmyard manure and other forms of organic substances produce good results.

Elements present in plants and coals

According to Professor G. Bertrand, a flowering lucerne plant contains the following elements :—

Carbon, hydrogen, oxygen, nitrogen, sulphur, phosphorus, chlorine, silicon, calcium, magnesium, potassium and sodium varying from 45.37 to 0.157% ; whilst the following elements are present in smaller amounts ranging from 0.0036 to 0.0000027%: iron, aluminium, boron, copper, zinc, manganese, fluorine, titanium, bromine, nickel, molybdenum, iodine and cobalt. Moreover, V. M. Goldschmidt and others have reported the presence of the following elements in coal :—

Carbon, hydrogen, oxygen, nitrogen, sulphur, phosphorus, chlorine, silicon, calcium, iron, manganese, sodium, potassium, titanium, zirconium, zinc, lead, cadmium, copper, gold, silver, vanadium, beryllium, germanium, nickel, barium, gallium, strontium, boron, scandium, yttrium, lanthanum, cobalt, molybdenum, uranium, arsenic, antimony, tin, iodine, bismuth, rhodium, palladium and platinum.

Elements present in soil

A fertile soil contains the following :—

Carbon, hydrogen, nitrogen, oxygen, phosphorus, potassium, calcium, magnesium, sodium, boron, copper, iron, manganese, zinc, cobalt, aluminium, titanium, molybdenum, chlorine, fluorine, iodine, sulphur and silicon. It is clear that for the healthy growth of a crop the soil must contain those elements which form essential ingredients of plant life.

From ancient times plant materials have been partially decomposed in heaps or in pits and converted into composts which are added to the fields as manure. The aim of composting is to conserve the nitrogen present in the plant materials and add it to the soil with about 10 times its weight of carbon in the form of humus which also contains most of the mineral matters present in the plant residues along with micro-organisms.

Since 1935, Dhar (Presidential address, National Academy of Sciences (India) 15th January (1937)) has emphasized that the direct addition of plant materials to the fields before composting is more beneficial to crops, because the energy materials like carbohy-

drates, celluloses, lignin, fats etc., when added to the soil, are partially oxidised and in this process nitrogen of the air is fixed. The value of the plant residues when added directly is due not only to their nitrogen content but also to the nitrogen fixed from the partial oxidation of their carbonaceous constituents. Hence much more humus (which is a combination of protein with lignin or cellulose or carbohydrate mixed with micro-organism) is formed and added to the soil when plant materials are mixed with the soil direct instead of their addition after composting elsewhere. The method of direct addition of plant materials to soils without composting has been adopted in farms in Pennsylvania and California, U. S. A. The citrus fruit industry in Palestine is utilising the direct addition of fruit and plant residues to the soil under the advice of Dhar in enriching the field.

The chief artificial fertilisers used in industrially advanced countries are potassium salts, phosphates and ammonium salts, urea and nitrates, and for acid soils, calcium carbonate. It is clear that the above fertilisers do not supply all the materials required for the healthy growth of a plant. On the other hand, plant residues when added directly, or as compost, supply all the materials needed for plant growth. Dhar and co-workers have shown that carbohydrates, celluloses, lignins and fats act as marked negative catalysts in the oxidation of proteins and ammonium salts or urea to nitrites and nitrates. Hence the proteins added along with plant materials liberate nitrate much more slowly for the benefit of the crop and for a longer period than ammonium salts or urea. The slow liberation of nitrates from humus decreases the chance of leaching away of nitrates from soil. It has been established in Allahabad that when 100 lbs of nitrogen are added to soil in the form of ammonium salts, 60 pounds are lost as nitrogen gas in three or four months without benefit to the soil or the crop/chiefly due to the formation and decomposition of the unstable substance, ammonium nitrite. Proteins also undergo oxidation and partially lose their nitrogen but in the presence of carbohydrates, celluloses, lignin and fats, the loss is slowed down and hence the crop can absorb the nitrate formed slowly for a longer period.

Nitrogen fixed with coal

We have observed that peat, lignite and bituminous coal when mixed with soil in a very finely divided condition are slowly oxidised and in this process fixation of nitrogen takes place. The amount of nitrogen fixed is greater in sunlight than in the dark. The estimated total nitrogen capital of the world peat and lignite is 47350 million tons. Moreover, the carbonaceous compounds present in coal are more inert than those existing in fresh plant materials, and hence, when finely divided coal is added to the soil, the available soil nitrogen is not readily converted into microbial proteins as with freshly added plant residues. Hence finely divided coal can be mixed with soil and crops can be grown almost immediately without giving any time interval which is needed when plant materials are added directly to the soil.

The growing of paddy and wheat has been found to be benefitted in our experiments by the addition of finely divided lignite and bituminous coal, which add nitrogenous manures and minerals needed for the growth of crops.

It is estimated that the nitrogen content of the humus in the top one foot of the cultivated lands of the world is 40000 million tons. The amount of nitrogen fixed in all the nitrogen industries of the world was 3.54 million tons in 1937. Hence the nitrogen still present in the world soils in the first foot from the top is 11250 times greater than the yearly nitrogen production. It is no wonder, therefore, that only 3 per cent of the world crop yield has been attributed to artificial nitrogenous manures in the last British Association meeting and reported in 'Nature', 1949 vol. 164, No. 4171, page 597, as follows :—

“At present only some 3% of the world food production can be attributed to the use of nitrogenous fertilizers. To raise the food by 10 %, that is to say one hundred million tons, involves a fourfold increase in supplies of fixed nitrogen at an approximate capital cost of £ 1,50,00,00,000. This would take a minimum of 15 years to achieve.”

It is interesting to note that even in the highly industrialized countries, the amount of nitrogen added per acre of land before the second World War, was much less than the nitrogen requirement of even one crop per year as shown below in pounds of nitrogen added per acre of land under cultivation :—

Belgium (28.5), Holland (24.8), Germany (15.6),
Denmark (10.3), Norway (6.0), Sweden (5.24), Italy (4.3),
France (4.0), Great Britain (2.5), U. S. A. (1.36),
Poland (0.73) and Hungary (0.15).

Summary and Conclusion

(1) Ammonium sulphate and ammonium phosphate lose the majority of their nitrogen content as nitrogen gas even in two months after their addition to the soil. With ammonium nitrate, ammonium tartrate, ammonium oxalate and ammonium citrate, urea, hippuric acid, gelatine, oilcake and blood, the loss is less within the same period. With oilcake containing fat, the loss is the least.

(2) With nitrogen rich compounds having a carbon/nitrogen ratio of less than 10, small quantities of humus are added to the soil and there is rapid loss of nitrogen in the gaseous state although they are quick acting nitrogenous manures.

(3) With plant materials, farmyard manure, cowdung, straw etc., with carbon/nitrogen ratio greater than 10, when added to the soil fixation of atmospheric nitrogen and humus formation take place and the addition of humus is much greater than when such substances are added after composting them elsewhere. It has been observed that the greater the carbon/nitrogen ratio of the starting material, the greater is the nitrogen fixation and increase of humus. This is the chief source of soil nitrogen.

(4) Much more nitrogen is fixed in the arable soils of the world by absorption of the solar light per year than the nitrogen fixed in all industrial operations.

(5) Marked nitrogen fixation and humus formation take place both in light and dark under completely sterile conditions with cowdung, leaves of Neem plants (*Melia Azadiractta* Lina) and wheat straw although the process is slower than in unsterile state.

(6) The efficiency of nitrogen fixation in light in the presence of calcium carbonate with a culture of *Azotobacter* fed with mannitol is appreciably greater

than in the dark due to the absorption of light by calcium carbonate although the amount of carbon oxidised in light is slightly less than in the dark in some experiments.

(7) Soil humus formation and nitrogen fixation also take place with soluble carbohydrates, glycerol and fat.

(8) Nitrogen fixation and humus formation on adding organic matters are quicker and greater with sandy soils than in clay soils.

(9) There is no decrease of available nitrogen in tropical soils on adding sugars, starch or glycerol although the bacterial population markedly increases.

(10) There is an initial decrease of available nitrogen with celluloses, lignins and fats when added to the soil although there is increase of total nitrogen. There is also increase of bacterial population with these carbonaceous compounds.

(11) The greater the fixation of nitrogen and humus formation in the soil, the greater is the residual effect of a manure.

(12) Humus liberates nitrates more slowly than ammonium salts and other quick acting manures and benefits the crop for a longer period. This explains why the nitrogen status of a soil is not improved without the addition of carbon compounds.

(13) The percentage of nitrogen in humus of tropical soils is greater than the percentage of nitrogen in soils of temperate countries. Acid soils have higher and alkaline soils lower carbon/nitrogen ratios than normal soils.

(14) Peat, lignite, brown coal, bituminous coal and anthracite coal have higher carbon/nitrogen ratio than normal soils. The higher the rank of the coal, the greater is the carbon/nitrogen ratio except lignite which usually contains less nitrogen than bituminous coal.

More acidic coals like acid soils have greater carbon/nitrogen ratios than less acidic coals.—

(15) Considerable quantities of humus are present in peat, lignite and coal. These materials improve crop production by their slow liberation of nitrate and fixation of atmospheric nitrogen. These are also beneficial to alkaline soils.

(16) Colloidal carbon is present in humus and coal and this causes the black colour.

(17) The same elements which are present in plants are also present in coal.

(18) The method of direct addition of plant materials without composting is easier and more profitable as there is nitrogen fixation and more humus formation than composting and has been adopted in Pennsylvania and California, U. S. A. and by the citrus fruit industry in Palestine.

(19) The estimated total nitrogen content of the world peat and lignite is 47350 millions of tons. The nitrogen content of the humus in the first foot of the arable lands of the world is believed to be 40,000 million tons and the world production of fixed nitrogen in factories was 3.54 million tons in 1937, that is, the soil nitrogen is 11,250 times greater than the fixed nitrogen production per year.

(20) Only three per cent of the world food production has been attributed to artificial nitrogenous manures.

(21) The pounds of nitrogen added per acre of land under cultivation varies from 0.15 in Hungary to 28.5 in Belgium and is much less than that required for the production of one crop per year.

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